

NANOCHAIN OF BUNDLED CARBON MOLECULES
USEFUL FOR HYDROGEN STORAGE

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Research and Development

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Related Applications

This application claims the benefit of U. S. Application S/N 60/151,527 filed on August 30, 1999, and incorporated herein by reference.

Background of the Invention

This invention relates to a form of carbon molecules useful in the storage of gas, such as hydrogen, and a process for making the carbon molecules.

There is much interest in materials suitable for the storage of gases such as hydrogen. Hydrogen is of particular interest in that it is an energy source having a high energy density per unit weight. Further, hydrogen burns cleanly and can be used in highly efficient fuel cells. However, since hydrogen gas is highly volatile, developing safe storage mechanisms has been an obstacle in the commercialization of hydrogen-based energy sources. As a result, there has been much study directed towards materials and methods directed towards the storage of large volumes of hydrogen.

Hydrogen storage is discussed in U.S. Patent No. 4,716,736 to Schwarz which is incorporated herein by reference in its entirety. A potential role of carbon nanofibers has also been widely discussed in the literature. One such review can be found in an article by N. M. Rodriguez entitled "A Review of Catalytically Grown Carbon Nanofibers", J. Mater. Res., Vol. 8, No. 12, December, 1993, pp. 3233-3250 which is incorporated herein by reference.

In a recent article entitled "Hydrogen Storage in Graphite Nanofibers" in *The Journal of Physical Chemistry, B.*, Vol. 102, No. 22, May 28, 1998, incorporated herein by reference, a graphite material is reported which purports to comprise a plurality of platelets of 300-500 angstroms in width which are stacked in a multilayered configuration. The material has been reported to have a high hydrogen storage capacity.

Additional carbon-based hydrogen storage compositions can be found in U.S. Patent No. 5,385,876 to Schwarz et al., U.S. Patent No. 5,653,951 to Rodriguez et al., U.S. Patent No. 5,846,639 to Robinson et al., U.S. Patent No. 5,837,741 to Schwarz et al., which are all incorporated herein by reference.

While the above references address materials and methods which are useful for producing carbon materials which may have hydrogen storage capabilities of varying degrees of effectiveness, there remains room for variation and improvement within the art of carbon species having useful gas storage properties.

Summary of the Invention

In accordance with the present invention, there is provided a composition and a process of making the composition comprised of:

a bundle of long chain carbon molecules having a surface area of approximately 13,740 m²/g, a density of about 1.31 gm/cc and a hydrogen adsorption capacity of approximately 30-50 percent by weight.

One aspect of the invention is a process of making the linear carbon chain molecules comprising the steps of providing a hydrocarbon source; mixing the hydrocarbon source material with an inert gas; supplying a single crystal membrane having a receiving surface and a discharge surface; introducing the mixed hydrocarbon and inert gas to the receiving surface of the single crystal membrane at a temperature of about 500-800°C; dissolving carbon atoms into the single crystal membrane; forming a reaction product along the discharge face of the single crystal membrane, the reaction product comprising a mixture of single chain carbon filaments

(nanochain), filaments of bundled nanochains and a crystalline carbon product.

It is yet another aspect of this invention to take the crystalline carbon product and disrupt the product by chemical or mechanical means to bring about a disassociation of the crystalline product into additional carbon nanochains. The disassociation of the carbon crystals in carbon nanochains is believed to increase the gas storage capabilities.

It is a further object of the present invention to provide a single crystal membrane which is soluble to carbon and further provides the ability to bring about the generation of organized, directional single chain filaments of carbon.

It is yet an additional aspect of the present invention to provide a composition comprising an effective amount of carbon nanochains so as to achieve a hydrogen storage material capable of sorbing at least about 20% by weight hydrogen relative to the carbon nanochain.

Brief Description of the Drawings

Figure 1 is a pictorial model of a conventional graphite sheet;

Figure 2 is a pictorial drawing similar to Figure 1 showing hydrogen bonding to the graphite sheet;

Figure 3 is a pictorial representation of a bundle of individual nanochains of carbon as provided by the present invention;

Figure 4 is a depiction similar to Figure 3 showing the adsorption/absorption of hydrogen with respect to the individual bundles of carbon filaments;

Figures 5 and 6 are schematic representations of an apparatus and process for carrying out the production of carbon nanochains;

Figures 7-11 are transmission electron micrographs of the reaction product comprising a mixture of crystalline carbon and carbon nanochains.

Detailed Description of The Invention

Reference now will be made in detail to the embodiments of the invention, one or more examples of which are set forth below. Each example is provided by way of explanation of the invention, not limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment, can be used on another embodiment to yield a still further embodiment. Thus, it is intended that the present invention cover such modifications and variations as come within the scope of the appended claims and their equivalents. Other objects, features, and aspects of the present invention are disclosed in the following detailed description. It is to be understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only and is not intended as limiting the broader aspects of the present invention, which broader aspects are embodied in the exemplary constructions.

In describing the various figures herein, the same reference numbers are used throughout to describe the same material, apparatus or process pathway. To avoid redundancy, detailed descriptions of much of the apparatus once described in relation to a figure is not repeated in the descriptions of subsequent figures, although such apparatus or process is labeled with the same reference numbers.

The present invention is directed to a fiber structure of linear carbon chain molecules which may have a chain length ranging from 2 carbon atoms to a chain length approaching 1 billion carbon units. The linear carbon chain molecules are preferably aggregated into bundles as set forth in Figures 3 and 4. In the preferred aggregation, the gas storage sorption capabilities for hydrogen is on the order of 30-40 weight percent hydrogen based upon available nanochain (one dimensional carbon molecules) surface area.

As seen in reference to Figs. 3 and 4, one dimensional carbon molecules (nanochains) 10 can be constructed which have a high sorbing

properties for hydrogen gas 20. The carbon nanochains 10 are produced at high temperature gaseous phases as best described below. The resulting chain molecule has about 10 times the surface area of graphite and is referred to as a "nanochain" in that the chain molecules of one dimensional carbon molecules aggregate to form bundles. The calculated data for the nanochain structure indicates it has a theoretical surface area of 13,740 m²/g which is approximately 10 times greater than that of conventional graphite. A highly purified nanochain structure would permit an adsorption value for hydrogen of approximately 30-50 percent by weight. A conventional graphite material 15 may be seen in reference to Fig. 1 and as further seen in Fig. 2 binding hydrogen molecules 20.

The density of the carbon nanochain is calculated to be 1.31 grams/cc. This value is significantly lower than reported values of amorphous carbon fibers, graphite, and nanofibers and is one way of distinguishing and characterizing the novel material from conventional forms of carbon.

The structure of the nanochain is produced via a catalyst-derived event in which a suitable hydrocarbon such as C₂H₂, C₂H₄, CH₄, or a mixture thereof is contacted with a high temperature single crystal catalyst such as Ni or Ni-Cu alloys at a temperature range of 500-800°C. The gaseous hydrocarbons are decomposed to H₂ and carbon wherein the carbon is dissolved into the catalyst where it diffuses through the catalyst and exits the surface of the catalyst. The catalyst membrane 30 may be used to form carbon chains 10 on the catalyst surface opposite the supply of high temperature gas. The linear chain molecules which exit the catalyst may be a carbon suboxide (C₃O₂, C₅O₂, and C_nO₂, where "n" is an odd number) or a linear carbon chain without oxygen. As indicated in Fig 6, reference character "X" may comprise a carbon molecule or an oxygen molecule. Producing linear chains of carbon which have terminal oxygen molecules at both chain ends is believed to provide nanochains that have a stable

resonance form. In this form it is believed that adjacent cumulenenic nanochains will interact by van der Waals' forces.

Conventional mechanisms using catalyst-derived processes would typically produce graphite at this stage. However, a preferred mode of the present invention provides deactivated regions 35 which limits the exit sites on the catalyst surface such that each exit site, on average, is a spaced distance from the next adjacent site. As best seen in reference to Fig. 6, carbon atoms exiting a partially deactivated catalyst can only interact with the next exiting carbon atom, thereby forming a chain structure as opposed to graphite plates. As a result, the novel nanochain structure may be prepared, the carbon chains forming bundles of carbon nanochains.

The deactivated regions 35 present on the catalyst may be limited by selective partial surface deactivation on one or both surfaces of the catalyst. One such method may use contamination of the catalyst with sulfur.

The partial contamination provides a fewer number of catalyst exit sites which, on the average, are spaced sufficiently apart from adjacent sites such that carbon atoms exiting the catalyst will interact only with the next exiting carbon atom. Alternatively, the partially deactivated catalytic membrane could comprise a heterogeneous material of a catalyst with inert (carbon impermeable) material to achieve a similar desired pattern of discrete, spaced nucleation sites for the forming carbon nanochains. The density and spacing of the catalyst exit sites also influences the number of chains in a bundle.

The nanochain structure is unique and quite distinct from previous carbon-based hydrogen storage materials. The unique structure is believed to contribute greatly to hydrogen storage capabilities of the resulting reaction product. The process of modifying the catalyst surface so as to limit the reaction sites is also different and distinct from techniques known within the art. Variations of this catalyst site nucleation control offers opportunities to develop and evaluate additional novel carbon-based structures.

A composition comprising a nanochain structure described herein is believed useful in its ability to absorb hydrogen. Accordingly, hydrogen storage vessels may be provided with the use of the nanochain bundle composition as the hydrogen storage material. The release and absorption of hydrogen can be carried out through variations in temperature and pressure similar to techniques well known in the art and as used with graphite-based hydrogen storage compositions. Suitable pressure vessels, housing the nanochain composition of the present invention, may be provided similar to those discussed in the references cited herein and as we well know within the art.

It is believed that small amounts of a nanochain-type structure may be produced along with graphite and other related carbon compositions. The presence of small amounts of the nanochain in an unpurified graphite composition may increase hydrogen storage for nanochain containing compositions. Accordingly, directing the catalyst conditions so as to increase the percentage of the nanochain structure, combined with post-production purification techniques, will enable a purified nanochain structure having enhanced hydrogen storage capabilities. The surface area of the nanochain structure is many times greater than that for a graphite. The nanochain structure provides a high surface area that directly relates to the hydrogen storage capacity of the nanochain structure.

Example 1

As seen in Fig. 5, a feed gas 40 comprising a mixture of 80% Argon and 20% methane is introduced at a supply pressure of 800-1000 torr to a reaction vessel 42. The reaction vessel 42 is in fluid communication with the feed gas supply 40. A reaction vessel outlet 44 was fitted with a gasket having a 2.0 ml thick single crystal nickel membrane 30 which blocks the normal flow of the feed gas at ambient temperatures and at the starting reaction pressure. A heater 46 was used to raise the temperature of the single crystal nickel membrane to 800°C prior to the introduction of the feed gas. For purposes of illustration, the reaction vessel 42 is shown detached from the outlet 44 that is designed to be threadably mated thereto. The outlet 44 is in further communication with a collection vessel 48. If desired, collection vessel 48 and outlet 44 may be in communication with an exhaust line through which analysis of any gaseous components may be conducted. A thermocouple 50 is used to monitor the reaction temperature in proximity to the single crystal membrane 30.

The nickel membrane, at the reaction temperatures used, allows the disassociation of the methane to molecular carbon and hydrogen gas. The single crystal membrane 30 is diffuseable to atomic carbon and impermeable to the hydrogen gas, the hydrogen gas being evacuated through an exhaust stream 52. The carbon is allowed to diffuse through the membrane for 24 hours at which time the system was de-energized and allowed to cool to ambient temperatures.

The supply side of the membrane 30 was discolored and had surface deposits of amorphous carbon as determined by SEM and EDX analysis. The product side of the membrane was covered in a black reaction product. EDX analysis reveals the reaction products consist only of nickel and carbon. TEM photographs, as set forth in Figs. 7-11, reveal numerous nickel particles N coated with crystalline layers C of carbon.

Outer edges of the crystalline layers revealed numerous regions of filamentous material F which extends from the surface of the layers C.

As seen in reference to the electron micrographs, the reaction product comprises a mixture of nickel particles ranging in size from 50 to 200 nm which are covered in a crystalline carbon coating C similar to that described in reference to Nolan et al "Hydrogen Control of Carbon Deposit Morphology", Carbon, Vol. 33, No. 1, page 79-85, 1995 which is incorporated herein by reference.

As best seen in reference to Figs. 7-11, the outer edges of the carbon shell defines a series of visibly frayed edges F where smaller filamentous units of carbon are present. The dimensions and morphology of the carbon strands correspond to filaments and strands as reported in Okuyama et al "Vapor-Grown Atomic Filaments of Graphite" Applied Physics Letters, Vol. 76 No. 2 January 2000 pages 161-163 and which is incorporated herein by reference in its entirety.

While Applicants' present data is limited in terms of resolution of individual filaments of carbon, it is believed that the frayed edge portions noted in Figs. 7-11 represent and include a plurality of carbon nanochains and bundles of nanochains.

While not wishing to be limited by theory, it is Applicants' belief that the present process produces a series of individual carbon chains which grow in length by the sequential and addition of additional carbon atoms from the single crystal membrane catalyst. However, it is believed consistent with the present observations that upon cooling to ambient temperatures, the single nanochains interact to form the crystalline structures C prevalent throughout the Figs. 7-11. As such, it is envisioned that the crystalline structures may be altered to produce a larger percentage of nanochains and individual carbon chains.

For instance, concentrated nitric acid washes and or peroxide washes may be used to release the nanochain, contained in the crystalline carbon structures. Additionally, it is envisioned that rapid

temperature changes such as using liquid nitrogen or helium, may further disrupt the crystalline carbon shells which are produced so as to enhance the number and amount of carbon nanochains. Such disruptions may be done in the presence of gas so as to have favorable adsorption occurring as the filaments and nanochains are released.

As best seen in reference to Fig. 6, a schematic representation of the carbon chain formation is presented. As seen, the nickel membrane catalyst 30 allows the formation of filamentous strands 10 on the lower surface during the elevated process temperatures. Further, it is believed that by increasing the average spacing between each carbon filament, such as by a selective catalyst poison, inhibitor, or deactivator 35, the production of single chains of carbon filaments is enhanced. In other words, by minimizing the proximity of adjacent nanochain and chain producing sites, the tendency of the exiting carbon to react to form graphite or some other carbon species may be minimized. As a result, the increased yield of the desire nanochain carbon product can be achieved by the selective deactivation of a portion of the catalyst surface.

It is also believed that the use of a single crystal membrane promotes the formation of the single carbon chains. Unlike a polycrystalline membrane which gives rise to multiple directions of carbon flow, the single crystalline membrane contains a unique directional flow that is believed to promote the establishment of the desired chain formation.

These and other modifications and variations to the present invention may be practiced by those of ordinary skill in the art, without departing from the spirit and scope of the present invention, which is more particularly set forth in the appended claims. In addition, it should be understood that aspects of the various embodiments may be interchanged both in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is

not intended to limit the invention so further described in such appended claims.